Drying conditions were critical, for if the sample were dried at 95° for 14 hr., the product was converted to a different substance, m.p. 150–151°. This substance was not investigated further.

Anal. Found: C, 64.36; H, 6.95; N, 14.70.

o-Methylthioaniline (XIII). A mixture of 25.0 g. (0.21 mole) of *o*-aminobenzenethiol,[21] 28.4 g. (0.20 mole) of methyl iodide, and 10 g. of sodium hydroxide in 100 ml. of 50% ethanol was heated under reflux with stirring for 45 min. A major part of the ethanol was removed by distillation, and the resulting solution was extracted with ether. The combined ether extracts were washed with several portions of water to remove sodium iodide and then dried over Drierite. After the ether had been removed by distillation, the residual oil was distilled to give 15.7 g. (57% yield) of a light yellow, foul smelling liquid; b.p. 124° (14 mm.), n_D^{25} 1.6220, d_4^{25} 1.115, lit.[23] b.p. 234°. As the original report[23] of this compound did not include an analysis, this was carried out in respect to the present sample.

Anal. Calcd. for C_7H_9NS: C, 60.39; H, 6.52; S, 23.03. Found: C, 60.52; H, 6.38; S, 23.15.

Phenylurea of XIII. From the reaction of 1.39 g. (0.01 mole) of *o*-methylthioaniline with 1.19 g. (0.01 mole) of phenyl isocyanate, by heating the mixture on a steam bath as previously described, was obtained 2.48 g. (86% yield) of a crystalline product, m.p. 126–127°. Recrystallization from ethanol gave fine needles, yield 2.19 g. (85%), m.p. 129–131°. The analytical sample, prepared by a second recrystallization from ethanol, melted at 132.5–134°.

Anal. Calcd. for $C_{14}H_{14}N_2OS$: C, 65.09; H, 5.46; N, 10.85. Found: C, 65.13; H, 5.39; N, 10.82.

Phenylthiourea of XIII. The same procedure was followed as for the phenylurea except that 1.35 g. (0.01 mole) of phenyl isothiocyanate was used; yield 2.44 g. (89%), m.p. 168–169°. Recrystallization from ethanol gave 1.28 g. (47% yield) of fine needles, m.p. 168–168.5°.

Anal. Calcd. for $C_{14}H_{14}N_2S_2$: C, 61.28; H, 5.14; N, 10.21. Found: C, 61.23; H, 5.16; N, 9.98.

Acknowledgments. This investigation was supported by a grant (G1100) from the National Science Foundation. Appreciation is extended to the American Cyanamid Co., 30 Rockefeller Plaza, New York 20, N.Y., for a generous sample of *o*-aminobenzenethiol, which was employed in this work.

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[23] A. W. Hofman, *Ber.*, **20**, 1788 (1887).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF TENNESSEE]

Benzilic Acid Rearrangement of Carbon-14 Labeled 2-Methylbenzil

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Received February 19, 1958

2-Methylbenzil has been synthesized specifically labeled with carbon-14 in the carbonyl group adjacent to the unsubstituted phenyl ring. Rearrangement of the labeled 2-methylbenzil produces 2-methylbenzilic acid with over 97% of the labeling in the carboxyl group, indicating that in the rearrangement the unsubstituted phenyl group migrates almost exclusively. The relationship of this finding to the mechanism of the benzilic acid rearrangement is briefly discussed.

In connection with another problem[1] it was necessary to prepare 2-methylbenzil. Because of recent interest in the rearrangement of benzils,[2] the 2-methylbenzil prepared was labeled with carbon-14 and its benzilic acid rearrangement was examined.

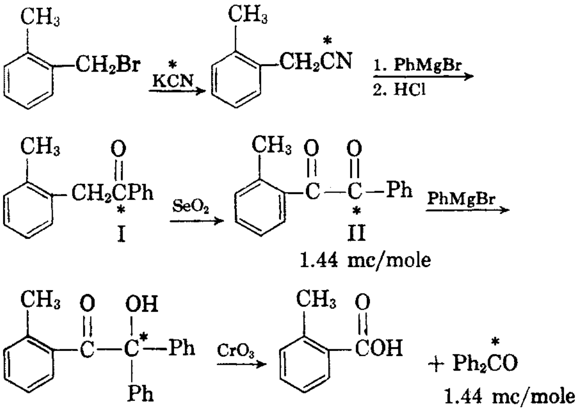

Chart I

Labeling of 2-methylbenzil with carbon-14 adjacent to the unsubstituted ring was effected by standard reactions shown in Chart I. The 2-methyldesoxybenzoin (I) intermediate in this preparation had not been previously prepared and was characterized by its reduction to a carbinol and also by its conversion to a 2,4-dinitrophenylhydrazone. The specificity of the labeling of the 2-methylbenzil (II) was checked by addition of phenylmagnesium bromide to this compound followed by oxidation of the resulting α-phenyl-2-methylbenzoin[1] to *o*-toluic acid devoid of radioactivity and benzophenone of the same molar radioactivity as the 2-methylbenzil (II).

Rearrangement of the labeled 2-methylbenzil in the usual manner afforded in good yield 2-methylbenzilic acid (III) of the same molar radioactivity as the benzil (II). The labeled acid (III) was oxidized with chromium trioxide to 2-methyl-

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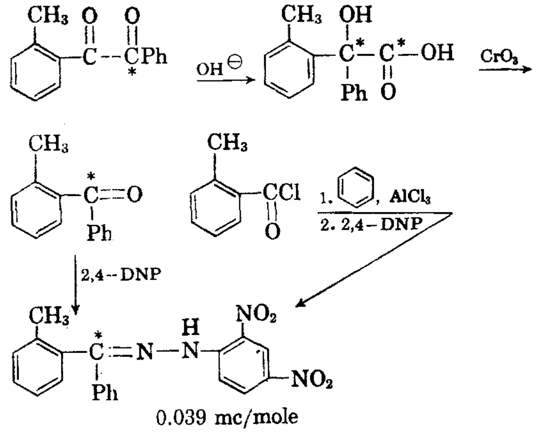
(1) J. F. Eastham, J. E. Huffaker, V. F. Raaen, and C. J. Collins, *J. Am. Chem. Soc.*, **78**, 4823 (1956).

(2) (a) W. von E. Doering and R. S. Urban, *J. Am. Chem. Soc.*, **78**, 5938 (1956); (b) M. T. Clark, E. C. Hendley, and O. K. Neville, *J. Am. Chem. Soc.*, **77**, 3280 (1955); (c) D. B. Ott and G. G. Smith, *J. Am. Chem. Soc.*, **77**, 2325, 2342 (1955); (d) J. D. Roberts, D. R. Smith, and C. C. Lee, *J. Am. Chem. Soc.*, **73**, 619 (1951); (e) W. von E. Doering, T. I. Taylor, and E. F. Schoenwaldt, *J. Am. Chem. Soc.*, **70**, 445 (1948).



IV

Chart II

benzophenone which was converted to a 2,4-dinitrophenylhydrazone (IV) for radioassay. The molar radioactivity of the 2,4-dinitrophenylhydrazone (IV) was just 2.7% of the starting benzil (II). Since IV had not previously been characterized it was also independently synthesized. These reactions are summarized in Chart II.

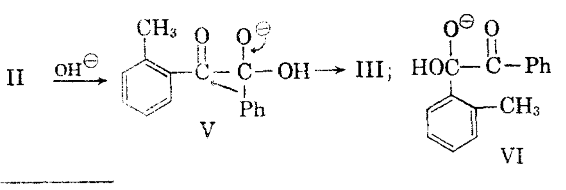
The findings shown in Chart II indicate that in the rearrangement of 2-methylbenzil the phenyl group migrates almost exclusively. In Table I this finding is compared with related results previously reported. In terms of the accepted mechanism for the benzilic acid rearrangement, the present finding shows that V, rather than VI, is the intermediate through which II is rearranged.[3]

TABLE I

MIGRATION IN THE BENZILIC ACID REARRANGEMENT

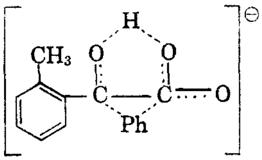
Compound	Per Cent Migration of Substituted Ring	Migration Ratio of Substituted Ring[a]
4-Methylbenzil	38.8[b]	0.63
2-Methylbenzil	2.7[c]	0.028
4-Chlorobenzil	67.2[b]	2.05
2-Chlorobenzil	31.2[d]	0.46

[a] Ratio of per cent migration of substituted ring to 100 minus this value. The ratios are not corrected for any isotope effect. [b] Ref. 2b. [c] This work. [d] Ref. 2c.



It is apparent that V should be much more stable than VI. Both by its electron release and by the steric compression it introduces, the *ortho* methyl group should destabilize VI. Destabilization of a similar intermediate by an *ortho* chloro (instead of methyl) group should be much less and it is therefore pertinent that the migration ratio of the substituted ring in 2-chlorobenzil is sixteen times that of the substituted ring in 2-methylbenzil (see Table I). It is also pertinent that the decrease in migration ratio of the substituted ring is much greater in going from 4- to 2-methylbenzil than it is in going from 4- to 2-chlorobenzil. These observations show the primary retarding effect of the *ortho* methyl group to be a steric one.

These observations are best explained with the assumption that the transition state for the benzilic acid rearrangement closely resembles expected intermediates such as V and VI, i.e., that the transition state lies quite close to the intermediate along a reaction coordinate leading from intermediate to product.[4] In other words we reject the proposal by Clark, Hendley, and Neville[2b] of a transition state, such as VII, with elaborately redistributed bonding electons.[5] If a transition state resembling VII were obtained, there could be little difference between the migration rate of a sterically encumbered group and an unsubstituted group; *o*-tolyl migration toward phenyl would have about the same steric requirements as phenyl migration toward *o*-tolyl.



VII

EXPERIMENTAL[6]

2-Methylbenzyl cyanide-C¹⁴. To a stirred solution of 55.5 g. of 2-methylbenzyl bromide in 200 ml. of absolute alcohol was added in one portion 22 g. of potassium cyanide (*ca.* 1.5 mc./mole) in 50 ml. of water. The reaction mixture refluxed spontaneously for a few minutes, was refluxed for 90 min., and was then allowed to stand at room temperature overnight. After the reaction mixture was treated with Norit-A and filtered through a pad of Fisher alumina, all of the alcohol was distilled at reduced pressure. The aqueous mixture remaining was extracted with ether which was in turn washed, dried, and evaporated. The residue was dis-

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(3) The first proposal of an intermediate similar to VI for the benzilic acid rearrangement was by A. Michael [*J. Am. Chem. Soc.*, **42**, 815 (1920)]. This concept of the key intermediate in the rearrangement has been investigated and refined[2] until today it is virtually incontrovertible. The last reported work[2a] substantiates this concept by showing rearrangement to be caused also by alkoxide ion (instead of hydroxide ion) in which case the product is the corresponding alkyl ester (instead of an acid).

(4) For a discussion of the possible relationship between transition states and known intermediates in a reaction see G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955).

(5) For other reasons other authors[2a] have criticized the proposal of Clark, Hendley, and Neville. It is important to note however that the latter stressed the tentative, speculative nature of their proposal.

(6) Melting points and boiling points are uncorrected. Microanalyses were performed by Weiler and Strauss, Oxford, England. Radioassays were performed by combusting samples to CO_2 and counting this in an ionization chamber with a vibrating reed electrometer.

tilled to yield 26 g. of 2-methylbenzyl cyanide-C^{14}, b.p. 95–96°/1 mm. (lit.[7] 115–120°/10 mm.).

2-Methyldesoxybenzoin (I). To the Grignard reagent prepared from 49 g. of bromobenzene and 7.6 g. of magnesium in 200 ml. of ether, there was added 20.5 g. of the above *o*-tolyl cyanide-C^{14} in 80 ml. of ether. The addition took about 20 min. during which time the stirred reaction solution refluxed spontaneously. The reaction solution was refluxed for 3 hr. and then poured onto a stirred mixture of 300 g. of ice and 150 ml. of concentrated hydrochloric acid. The aqueous layer was separated quickly and allowed to stand at room temperature overnight. This aqueous mixture was then extracted with ether which was in turn washed, dried, and evaporated to leave 11.6 g. of a crystalline residue, m.p. 60–65°, which could be used for oxidation to 2-methylbenzil (see below) without further purification. Purification of the crude desoxybenzoin was attempted by distillation (b.p. 170–175°/8 mm.), crystallization, and sublimation. The latter process gave material with a sharp m.p., 65.5–66°, but this material did not give the proper elemental analysis for 2-methyldesoxybenzoin. For characterization the compound was reduced to 2-methylbenzylphenylcarbinol (see below) and converted to a 2,3-dinitrophenylhydrazone.

To a solution of 47 mg. of 2,4-dinitrophenylhydrazine in 0.25 ml. of concentrated sulfuric acid there was added a solution of 50 mg. of the 2-methyldesoxybenzoin (m.p. 65–66°) in 2 ml. of 95% alcohol. The mixture was refluxed 10 min., cooled, and the red needles which appeared collected. Recrystallization of this product from alcohol then from chloroform gave 57 mg. of *2-methyldesoxybenzoin 2,4-dinitrophenylhydrazone*, m.p. 182–183°.

Anal. Calcd. for $C_{21}H_{18}N_4O_4$: C, 64.60; H, 4.65; N, 14.35. Found: C, 64.54; H, 4.76; N, 14.30.

2-Methylbenzylphenylcarbinol. A solution of 40 mg. of lithium aluminum hydride and 210 mg. of 2-methyldesoxybenzoin (m.p. 65–66°) in 20 ml. of ether was refluxed for 10 min. Work up in the usual manner gave an oil which crystallized from ligroin as 2-methylbenzylphenylcarbinol, m.p. 29–30°.

Anal. Calcd. for $C_{15}H_{16}O$: C, 84.87; H, 7.60. Found: C, 84.67; H, 7.81.

2-Methylbenzil-C^{14} (II). A solution of 6 g. of crude 2-methyldesoxybenzoin-C^{14} (m.p. 60–65°), 3.2 g. of selenium dioxide, and 0.5 ml. of water in 20 ml. of dioxane was refluxed for 12 hr. The reaction mixture was filtered and the solvent was distilled. The residue was leached with ether and the resulting ethereal solution was washed, dried, and evaporated to an oil which was distilled; the fraction collected 175–185°/3 mm., 4.2 g., crystallized spontaneously. Recrystallization gave pure 2-methylbenzil, m.p. 57–57.5° (lit.[8] 57–58°), 1.442 ± 0.001 mc./mole.

α-Phenyl-2-methylbenzoin-C^{14}. A Grignard reaction between the above-labeled benzil and phenylmagnesium bromide was carried out exactly as described[1] for the unlabeled benzil. There was produced carbinol-labeled α-phenyl-2-methylbenzoin-C^{14}, m.p. 116–117°, 1.442 ± 0.003 mc./mole. Oxidation of a sample of the carbinol-labeled benzoin was carried out with chromium trioxide, again exactly as described[1] for the unlabeled benzoin. There was produced *o*-toluic acid, m.p. 104–105°, which was devoid of radioactivity, and benzophenone which was characterized as its 2,4-dinitrophenylhydrazone, m.p. 238–239°, 1.441 ± 0.002 mc./mole.

2-Methylbenzilic acid-C^{14} (III). A solution containing 130 mg. of 2-methylbenzil, 550 mg. of potassium hydroxide, 1 ml. of alcohol, and 1.5 ml. of water was heated for 10 min. on the steam cone. The solution was cooled, diluted with water, and extracted with ether. There was recovered 29 mg. of 2-methylbenzil from this ether extraction of the reaction mixture. The aqueous layer was acidified and extracted with ether. This ether extract was dried and evaporated and the residue recrystallized to give 105 mg. (96% based on unrecovered starting material) of 2-methylbenzilic acid C^{14}, m.p. 113.5–114.5° (lit.[9] 114.5°), 1.443 ± 0.001 mc./mole.

Degradation of 2-methylbenzilic acid-C^{14}. A solution of 99 mg. of 2-methylbenzilic acid and 31 mg. of chromium trioxide in 1 ml. of glacial acetic acid was heated on the steam cone for 30 min. with occasional swirling. Two milliliters of water were added and the solution was extracted with ether. The ether solution was extracted with saturated sodium bicarbonate solution and with water, dried and evaporated to give 74 mg. of a light yellow oil. A solution of this oil and 74 mg. of 2,4-dinitrophenylhydrazine in 1 ml. of concentrated sulfuric acid and 0.25 ml. of ethanol was heated for about 30 sec. on the steam cone, then the total volume was increased to 5 ml. by the addition of 95% ethanol. This solution was refluxed for 20 min., during which time red crystals began to appear. The mixture was cooled and centrifuged and the liquid decanted. The red crystals were washed with water and recrystallized five times from a mixture of equal portions by volume of chloroform and alcohol. There was obtained 86 mg. of 2-methylbenzophenone 2,4-dinitrophenylhydrazone, m.p. 176–178° (undepressed by authentic material prepared as described below), 0.039 ± 0.001 mc./mole.

2-Methylbenzophenone 2,4-dinitrophenylhydrazone (IV). A mixture of 20 g. of 2-methylbenzoyl chloride, 20 g. of anhydrous aluminum chloride, and 50 ml. of dry benzene was refluxed for 1 hr. The excess benzene was removed by distillation and the residue was distributed between water and ether. The ether layer was washed with aqueous hydrochloric acid, aqueous sodium carbonate and water, dried, filtered and the ether distilled. The residue was distilled; the fraction distilling at 121.5–122.5°/1.25 mm. amounted to 14 g. of crude 2-methylbenzophenone as a light yellow oil. A sample of this oil was treated with 2,4-dinitrophenylhydrazine in ethanolic sulfuric acid in the usual manner. 2-Methylbenzophenone 2,4-dinitrophenylhydrazone was obtained as red needles, m.p. 176–178°.

Anal. Calcd. for $C_{20}H_{16}N_4O_4$: C, 63.85; H, 4.25; N, 15.42. Found: C, 64.15; H, 4.38; N, 14.84.

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(7) P. Hill and W. F. Short, *J. Chem. Soc.*, 1123 (1935).

(8) A. McKenzie and A. L. Kelman, *J. Chem. Soc.*, 412 (1934).

(9) K. Mislow and M. Siegel, *J. Am. Chem. Soc.*, 74, 1060 (1952).